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Temperature variation of diamagnetic susceptibility of graphite

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The first observations on the magnetic properties of graphite were made by Krishnan and Ganguly (1939), followed by a number of other workers (Pacault and Merchand 1955, Pinnik 1954, Berlincourt and Steele 1955). The interesting feature of the experimental results, which are in general agreement with each other is that graphite has a very large diamagnetic susceptibility almost wholly confined along the c-axis. The observations and discussions on the magnetic susceptibility of graphite are, therefore, confined to the property along the c-axis. At low temperatures the susceptibility shows a very feeble dependence on temperature. According to Krishnan and Ganguly (1939) the susceptibility tends to attain a temperature-independent value at low temperatures. Pacault and Marchand (1955) could successfully apply Landau-Peierls formula to explain the temperature variation of magnetic properties of graphite. However, their relation was derived on the assumption of the number of free carriers in graphite to be constant at all temperatures, which is contrary to the findings of other observers (Kinchin 1953, Primak and Fuchs 1954) including the present authors according to whom the number increases with temperature. It is, therefore, necessary to see whether the temperature variation of susceptibility can be explained taking into consideration the increase in the number of free carriers with temperature. We have measured the temperature variation of $\chi_{\parallel}$ of Ceylon graphite (Figure 1). The method of experiment is the same as that in use in this laboratory (Guhathakurta and Bose 1970).

In the present experimental observation also it is seen that we can divide the temperature variation of the susceptibility into two regions. There is a region where $\chi_{\parallel}$ is almost temperature independent and then it decreases as the temperature is increased. This is in agreement with the previous observations. Applying Landau-Peierls relation, it is found that

$$\chi = \frac{n\mu_B^2}{3kT}\{6-(\alpha_e^2+\alpha_h^2)\} \tag{1}$$

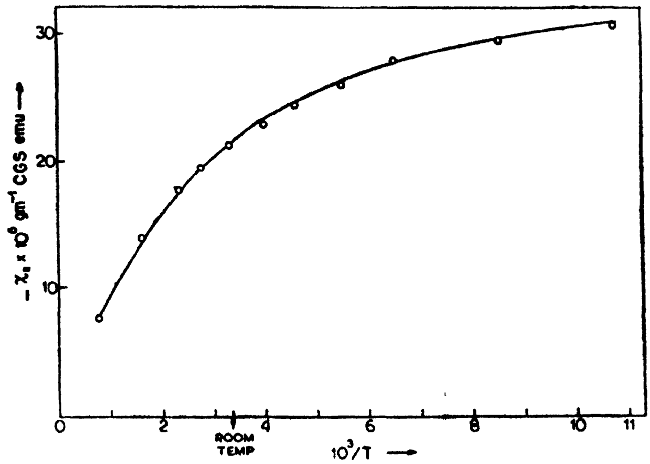

Figure 1. Temperature variation of diamagnetic susceptibility of graphite.

where the symbols have usual significances ; $n_e = n_h = n$, α_e and α_h are inverse of effective masses of electrons and holes respectively.

Let us now make a calculation for χ using the values of n, α_e and α_h obtained by different workers [Kinchin (1953), Barlincourt and Steele (1955), Maclure (1957) etc.]

$$n \approx 2 \times 10^{18}$$

$$\alpha_e^2 \approx 771.6$$

$$\alpha_h^2 \approx 204$$

The above values give $\chi_e \approx 1.2 \times 10^{-6}$ CGSemu where as it is well-known that the observed values of $\chi_\parallel$ at room temperature is $\approx 22.5 \times 10^{-6}$ CGSemu. Thus, it is found that the value of the susceptibility of the free electrons is a small fraction of the observed diamagnetic susceptibility of graphite and can not therefore account for the large value of the susceptibility.

It is known that

$$\chi = \chi_L + \chi_i(0) + \chi_i(T) + \chi_o(T) \tag{2}$$

where

χ_L = temperature independent contribution from core electrons and electrons in valence band (Mansfield 1959)

$\chi_i(0)$ = temperature independent contribution to the susceptibility from any neutral impurities that may be present

$\chi_i(T)$ = temperature dependent susceptibility due to paramagnetic impurities (if any)

$\chi_c(T)$ = magnetic susceptibility due to free carriers (electrons and holes)

The large diamagnetism is due to χ_L and the free electrons and holes of low effective mass i.e. $\chi_c(T)$.

Adams II (1953) has shown that when in a substance the Brillouin zone is almost filled with electrons and the next upper zone is almost empty, large diamagnetic susceptibility would arise due to (i) the filled states near the boundary of the zone and (ii) the unfilled states outside the zone when the energy difference between the states across the boundary of the zone is very small and the value of the effective mass for both these states are also small. In case of graphite it is well-known that the valence band and conduction band in the substance are just touching each other or they slightly overlap (Wallace 1947). Also that the effective mass for both these states are small. From the above calculation for the diamagnetic susceptibility of free carriers (electrons+holes) of graphite it is evident that the main contribution to the large susceptibility comes from χ_L. This is also consistent with the idea of Adams II (1953). We, therefore, try to explain the temperature variation of χ_l of graphite taking help of the idea of Adams II (1953).

It would be noted here that as the temperature increases electrons from the valence band are excited to the conduction band and thus there is an increase in the number of free carriers (both holes and electrons). This will increase the value of the contribution $\chi_c(T)$ of eq. (2) but as shown in the previous calculation the value will still remain a small fraction of the observed susceptibility.

Let us now look at the nature of χ_L. As stated earlier, the term which has been taken to be temperature independent is the diamagnetic contribution of the core electrons and valence electrons. The valence electrons concerned here are those which are not free carriers. These, therefore, contribute to the temperature independent diamagnetism which will be proportional to the number of such electrons in the valence band. Due to the excitation of electrons mentioned above the number of electrons in the valence band which are not free carriers (i.e. which contribute to χ_L) decreases and therefore χ_L will deccrease. This means χ_L shows an indirect dependence on temperature. This dependence is indirect because so long as the number of electrons in the valence band is constant, χ_L is independent of temperature. Whereas in case of free electrons even if the number of free carriers is fixed, the susceptibility decreases with temperature (cf. eq. (1)).

The consequence of the above contention will be that (i) the free electrons thus excited to the conduction band and holes in the valence band will contribute to magnetic susceptibility $\chi_c(T)$ according to Landau Peierls formula as given in eq. (1), (ii) a decrease in the diamagnetism through the decrease in the contribution from the valence electrons which happens due to a decrease in their number. This means χ_L which is generally thought to be temperature independent is not so.

If the decrease in χ_L is more than compensated by the diamagnetic contribution $\chi_0(T)$ of the free carriers then the substance will show an increase of diamagnetic susceptibility with temperature. In large band gap semiconductors such behaviour is observed because the band gap being large the diamagnetic contribution of the valence electrons to χ_L is small. Since in graphite the value of ΔE is very small the rate of increase of free carriers n with temperature and hence the increase of $\chi_0(T)$ which depends on n/T will also be small. It has been shown earlier that the diamagnetism of graphite is almost wholly due to the diamagnetic contribution of the core and valence electrons. The decrease in the observed $\chi_\parallel$ can be accounted for if we consider the argument as stated above that χ_L decreases as electrons from valence band are thermally excited. Since χ_L is large the contribution of each electron in the valence band is also proportionately large and is larger than the diamagnetic contribution which this same electron makes when excited to the upper band as free carrier. Therefore, as more electrons are excited due to rise of temperature the observed $\chi_\parallel$ will decrease becouse the decrease in χ_{dia} for each excited electron from valence band is more than the increase of χ_{dia} due to this electron as free carrier in the conduction band. That χ_L sometimes shows a temperature dependence has also been observed in Ge (Krumhansal and Brooks 1956). Thus, the argument given above can account for the decrease in $\chi_\parallel$ with temperature.

At low temperature $\chi_\parallel$ is almost independent of temperature. This is because as the temperature is lowered the number of free carriers in the conduction band decreases and the electrons in the valence band increases making the diamagnetic susceptibility larger. At low temperature as the electrons in the conduction band becomes small, the change in the number of electrons with temperature also becomes small and thus $\chi_\parallel$ tends to a constant value.

It would be interesting to make a theoretical calculation for the magnetic susceptibility of valence electrons, which are not free carriers and compare it with the observed results. Unfortunately, no such attempt has been made so far.

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